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Nucleation in glasses – new experimental findings and recent theories

Laurent Cormier*

Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie, CNRS UMR7590, 4 place Jussieu, Paris 75005, France

Abstract

Nucleation is the initial process and the key operation to control and predict devitrification in glasses. The classical nucleation theory is widely used to describe qualitatively this phenomenom though it is well known that considerable discrepancies exist with experimental results. Recent theories have been developed (Generalized Gibbs Approach, two-steps model) to overcome the approximations in the classical model. They are based on experimental observations, considering explicitly non-classical pathways driving to the critical nucleus formation. Additionally to these models, it is important to obtain high quality experimental information below about 50 nm. Using scanning transmission electron microscopy in high angle annular dark field imaging mode (STEM-HAADF), we have evidenced that glass structure is mesoscopically inhomogeneous and that intrinsic heterogeneities play a key role for promoting nucleation.

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Keywords: nucleation; theory; aluminosilicate; STEM HAADF

* Corresponding author. Tel.: +33-1-44-27-52-39
E-mail address: cormier@impmc.upmc.fr

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1. Introduction

Crystallization mainly occurs considering two processes. It can appear when a liquid is slowly cooled down below the melting temperature, which is an aspect very important in Earth Sciences to understand texturation of igneous volcanic rocks or partitioning of elements between crystals and melts (Kirkpatrick, 1975). If we obtain a glass, we can also devitrify it by applying a thermal treatment above the glass transition temperature, T_g; this case is the usual process to form glass-ceramics. Both aspects can occur in the context of nuclear wastes. During glass elaboration, remaining unfused crystals or formation of crystals upon cooling has to be avoided. Crystallization can occur during the batch-to-glass conversion, by corrosion of the glass melter or close to thermal gradient zones that can be found in the cold crucible technology (Delattre et al., 2013). After pouring the glass into canisters, the radiogenic heat produced by High Level Wastes (HLW) induces slow cooling of the glass, which may promote formation and growth of crystalline phases and may represent 1-5 vol% of HLW (Jantzen et al., 2010). Some of the crystalline phases such as nepehline, acmite or lithium silicates can be problematic due to their low durabilities. Finally, glass–ceramics matrices are investigated as alternative waste forms for actinides immobilization (Loiseau et al., 2004). The presence of crystals is thus an important issue regarding the lifetime or the performance of the crucible, the glass durability and the partitioning of radionuclides into crystalline phases.

Crystallization is considered to be a two steps process: nucleation initiates the appearance of nuclei that can reach a critical size then growth corresponds to the increase in the size of these critical nuclei. Nucleation is the key step to control and predict devitrification in glasses. Though the Classical Nucleation Theory describes qualitatively well nucleation processes, it fails by many orders of magnitude in a quantitative prediction. A major limitation is the nucleation pathways, *i.e.* the evolution of the system leading to a critical nucleus. Glasses are well known to be non-homogeneous materials and phase separation has long been evoked has an initial step driving nucleation. However, comprehensive compositional or structural information below about 50 nm are scarce and the role between glass heterogeneities and nucleation is not well established. We present recent experimental investigation indicating that self-organization of the parent glass structure drives directly the crystallization and explains the efficiency of crystal formation in glass ceramics. Using scanning transmission electron microscopy in high angle annular dark field imaging mode (STEM-HAADF), a direct visualization of the glass organization shows that glass structure is intrinsically inhomogeneous and that these inhomogeneities are correlated with the pathways of nucleation. The mesoscopic organization of the glass structure implies that energetic barriers can be easily overcome to promote nucleus formation and crystal growth. These results are compared to the most recent models of nucleation that are presented in the following section.

2. Theories of nucleation

Nucleation can be understood simply with the Classical Nucleation Theory (CNT). Though imperfect, this theory allows an easy physical understanding of the main mechanisms. However, as it is difficult to predict nucleation rates with CNT, alternative theories have been proposed and some are becoming very popular and attractive during the last decade.

2.1. Classical nucleation theory (CNT)

CNT lies on different hypothesis known as the capillary approximation bonding the theory: (i) whatever its size the germ can be described with the same macroscopic properties than the stable crystalline phase that will form (*i.e.* same density, same structure, same composition and same thermodynamic properties); (ii) the initial germ is spherical with a radius r and a finite interface (to minimize the surface energy).

CNT predicts the stationary nucleation rate I(T), corresponding to the number of nuclei per time unit at a given temperature (Fig. 1a):

$$I_{st}(T) \propto \exp\left[-\frac{\Delta G_D}{k_B T}\right] \exp\left[-\frac{W^*}{k_B T}\right] \quad (1)$$

where k_B is the Botlzmann constant and T is temperature. The first exponential term is derived from kinetic consideration, describing the jump of an atom from the liquid to the surface of the crystal with an an activation energy for the diffusion ΔG_D. This activation energy is related to a diffusion coefficient D, which can, for reasons of simplicity, be simplified to a transport properties easily measurable, the viscosity, η, by using the Stokes-Einstein relation:

$$\exp\left(-\frac{\Delta G_D}{k_B T}\right) \propto D = \frac{k_B T}{3\pi\lambda\eta} \tag{2}$$

with λ the jump distance (~ twice the ionic radius). The second exponential in expression (1) describes the thermodynamic contribution. W* is the critical work of formation of a critical cluster r* determined by the maximum of the thermodynamic barrier ∂W / ∂r (Fig. 1b), where W is the free energy cost associated with the formation of a nucleus:

$$W = \frac{4\pi r^3 \Delta G_V}{3} + 4\pi r^2 \gamma \tag{3}$$

In expression (3), $\Delta G_V = G_l - G_c$ ($\Delta G_V < 0$) is the difference in free energy per unit volume and γ is the interfacial energy per unit area corresponding to the creation of a melt/crystal surface. For a cluster with a size larger than the critical radius r*, the favorable volume term begins to dominate the unfavorable surface term, thereby the nucleus becomes energetically stable and may grow.

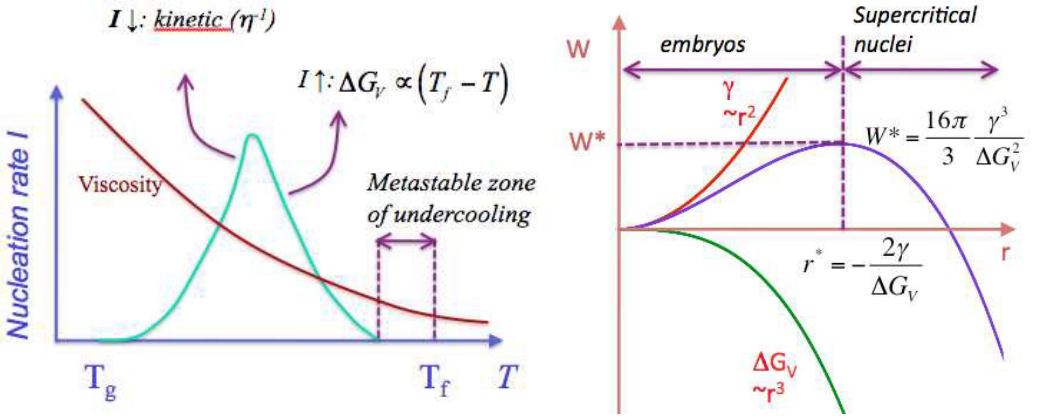

Fig. 1. (Left) Nucleation rate, I, as a function of the temperature. At high temperature, there is a metastable zone of undercooling where no stable nuclei can be formed because the surface energy is too important. As the temperature decreases, the volumic term ΔG_V dominates and nuclei can appear, favored by the increased in undercooling (T_f - T), until the viscosity increases, which counterbalances the termodynamic term and reduces the nucleation rate. (Right) Variation of the work of formation, *W*, and its surfacic and volumic components as a function of the nuclei size, *r*. Critical values r* and W* are also given.

In a similar way, we can obtain the rate of crystalline growth, C(T), that describes the growth of critical nuclei having radius larger than r*. We recognize in the expression (4) the thermodynamic component ΔG_V and the kinetic component ΔG_D:

$$C(T) = f\lambda\nu e^{-\frac{\Delta G_D}{k_B T}} \left[1 - e^{\frac{\Delta G_V}{k_B T}}\right] \tag{4}$$

with *f* the fraction of sites on the crystal surface which are available for attachment. ΔG_D is not necessarily identical to the activation energy for nucleation since growth requires long range diffusion, contrary to nucleation that implies short range diffusion near the crystal/melt interface.

The two curves I(T) and C(T) that can be determined experimentally are usually displaced in temperature explaining the two stage processes for fabrication of glass-ceramics: at temperature slightly above T_g, a first step induces the formation of a large amount of nuclei; at higher temperature, a second step allows the growth of the nuclei to form crystals of nanometer or micrometer size.

A description of I(T) by the CNT is qualitatively correct, which implies that CNT gets the physics underlying the process of nucleation. However, CNT fails by several orders of magnitude for a quantitative description of nucleation, resulting in severe underestimation of the nucleation rates (Sen and Mukerji, 1999). Various developments or alternative theories have been proposed mainly based on phenomenological or density functional methods (Granasy and James, 1999; Schmelzer et al., 2010; Schmelzer et al., 2004; Sen and Mukerji, 1999; Weinberg, 2002). They resolved some of the limits of CNT such as the use of the capillarity approximation, a sharp interface, a lack of temperature or size-dependencies for the interface or the surface energy. In the past decade, advances in experimental observations of the initial nucleation steps lead to further advances.

In the CNT, the critical nucleus is essential but no information of the pathways leading to its formation is given. It is simply assumed that random fluctuations occur in the liquid corresponding to clustering of atoms that adopt *simultaneously* a crystalline environment, which means a single order parameter. In the heart of the recent theories described below is the understanding of the pathways driving to the formation of nuclei.

2.2. Generalized Gibbs Approach (GGA)

The Generalized Gibb's approach (GGA) (Schmelzer et al., 2006; Schmelzer et al., 2004) is based on experimental observations showing that the structure and properties of the nuclei can deviate from those of the macroscopic phases. This is in good agreement with the Ostwald's rule of stages (Ostwald, 1897) and with recent experimental evidences (Chung et al., 2009). Ostwald proposes that the final stable state is reached via a discrete series of metastable states, for which a small energy barrier has to be overcome. In consequence, nuclei will change in composition and structure during the nucleation process (Fig. 2a). GGA is a modification of the CNT by introducing properly a change in composition for the nuclei.

Critical parameters (radius r* and work of formation W*) are similar to those obtained by CNT but are now depending of the composition of the nucleus α:

$$r^* = -\frac{2\gamma}{c_\alpha \Delta G_V} \quad \text{and} \quad W^* = \frac{16\pi}{3}\frac{\gamma^3}{\left(c_\alpha \Delta G_V\right)^2} \tag{5}$$

with c_α the volume concentration of the newly appearing phase. Therefore, the critical nucleus is defined not only as the maximum for W with respect to the cluster size but also as the minimum of W^* with respect to any composition allowed for the nucleus.

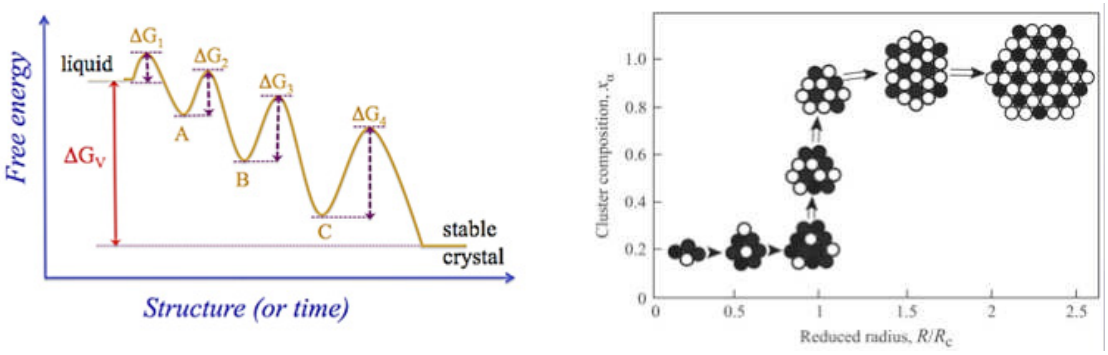

Fig. 2. (a) Schematic representation of the transformation considering different metastable intermediate states (A, B, C) before reaching the stable equilibrium state (adapted from (Chung et al., 2009)).; (b) Schematic scenario predicted by GGA (Schmelzer et al., 2010).

Contrary to CNT that predicts a continuous evolution of the size of the nucleus with a constant composition and structure corresponding to the final macroscopic phase, the GGA defines a different nucleus evolution (Fig. 2b). The size of the nucleus is changed up to the critical value with few changes in composition compared to the initial state. Then, at almost constant size, the composition and structure evolves towards the macroscopic phase that can further grow. The energy barrier is not overcome via a change in size (CNT) but via a change in composition. The work of formation with GGA is similar to that for CNT but as γvaries with the evolution of the state parameters of the critical nuclei, W^* is lower than predicted by CNT, leading to higher nucleation rates.

GGA shows several similitudes with the Density Functional Theory (DFT) developed by Cahn-Hilliard (Cahn and Hilliard, 1958). In particular, the GGA scenario corresponds to an amplification of composition (and structure) fluctuations leading to the macroscopic phase, which ressembles a phase separation. Contrary to CNT but in agreement with DFT, GGA shows that the work of formation tends to zero close to the spinodal and the theory can thus discriminate between a metastable and an instable state. They also both show a divergence of the critical radius near the spinodal, consistent with small density fluctuations but with large spatial extension. Another advantage of the GGA is that preferential pathways of the nucleus towards the new macroscopic phase depend of the diffusion coefficients of each element. This resolves a limit of the CNT concerning the validity of the Stokes-Einstein equation. Indeed at high undercooling (where nucleation occurs), experimental evidences exist for a decoupling between relaxation processes and diffusion (Gruener, 2001), so that the viscosity is no more a good approximation for the atomic transport properties (Roskosz, 2005b; Tarjus and Kivelson, 1995). This will require the knowledge of individual atomic diffusion coefficients, which is clearly a limit for the applicability of GGA for complex systems.

2.3. Two-steps model

In the case of crystallization of a solid from a liquid, the distinction of two different states requires at least two order parameters, for example the density and the structure. CNT considers that these two parameters elvolve simultaneously, which means that the nuclei should have instantaneously the density and the atomic organization of the final crystal. If the two order parameters are not evolving in the same time, CNT is not applicable and cannot describe correctly the pathways driving the nucleation.

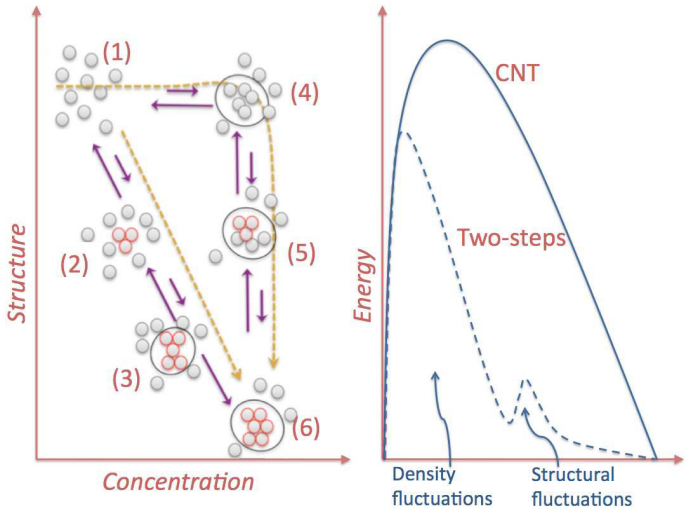

Fig. 3. (Left) Schematic representation of the two-steps model. In an initial homogeneous liquid (1), CNT predicts the formation of sub-critical nuclei by the clustering of structural units (2), until reaching the critical nuclei (3). Both sub-critical and critical nuclei have directly the structure of the final crystal (6). On the contrary, the two-steps model suggests a first step with the formation of a dense disordered phase (4). In the second step (5), inside the dense droplets, a structural reorganization occurs forming the first crystals. (From (Vekilov, 2010)). (Right) The two energy barriers to overcome in the two-steps model are lower than the single energy barrier in CNT (From (Lutsko and Nicolis, 2006)).

The two-step model is based on experimental observations and simulations that evidence density fluctuations and structural fluctuations that are separated in time, especially close to the liquid-liquid separation (Talanquer and Oxtoby, 1998; ten Wolde and Frenkel, 1997; Vekilov, 2004). In this model, two successive stages are considered (Fig. 3). The first step is the local formation of a disordered region different to that of the initial liquid phase, typically droplets with higher density. In the second step, within this region, a structural reorganization leads to the appearance of crystals. The dense region surrounding the first crystals could by wetting lower the surface energy compared to an interface crystal-initial phase (ten Wolde and Frenkel, 1997), though this point is still controversial (Vekilov, 2004).

Simulations based on the DFT (Lutsko and Nicolis, 2006) have compared the pathways from the CNT and the two-step model. They have shown that each step in the two-step processes corresponds to a low energy barrier, so that the sum of these two barriers requires less energy to surmount the unique CNT barrier (Fig. 3). The consequence is that this pathway is favored and the nucleation rate is higher.

Another interesting experimental aspect is that the limiting factor is the second step, *i.e.* the structural reorganization within the dense liquid region (Filobelo et al., 2005), illustrating the importance of the atomic diffusion and of the kinetic in the nucleation mechanism.

2.4. Nucleation and phase separation

As explained in section 2.2, GGA shares similitudes with a spinodal decomposition, *i.e.* a process via continuous amplification of differences in density and/or composition. The phase that is appearing corresponds to a saddle point in the thermodynamic potential landscape. Such a scenario is adapted for initial states close to the binodal curve and in the central part of the metastable region. However, close to the spinodal curve, the thermodynamic barrier is small and tends to zero whereas the critical radius increases and tends to infinity. In order to evolve towards the new phase through the saddle point, nuclei with large spatial extent must be formed, which is unfavorable. Instead, the nuclei follow a pathway passing through a ridge point of the thermodynamic potential, corresponding to nuclei with smaller radii (Abyzov et al., 2010).

In the two-step model, the liquid-liquid (L-L) separation is also important. When the system is below the L-L separation, the dense liquid phase is stable relative to the initial liquid, but metastable relative to the crystalline

phase. Again, the energy barrier can vanish close to the spinodal domain. When the system is above the L-L separation, the dense liquid phase is metastable relative to the initial phase and the final crystalline phase, thereby corresponding to a density fluctuation of short life time. Around the critical point of the L-L separation, density fluctuations of large amplitude could be the first step of nucleation, the second one being the formation of the crystalline atomic order. In the multicomponent glasses, the first stage comes along probably with chemical diffusion.

2.5. GGA and two-step model

These two methods are probably not irreconcilable and present strong analogies. They are both based on a better understanding of the pathways driving the formation of the critical nuclei and on the presence of an intermediate metastable state. GGA presents a first stage where a phase grows in size (nothing forbids that in this intermediate stage the germ be disordered or ordered), followed by a second stage where the aggregate with critical size reorganizes towards a periodic structure. A second important similitude, still not yet well understood, is that these two theories are intrinsically linked with the phase separation phenomenon. However, a severe limit in these models is their applicability to chemically and structurally complex systems as encountered in nuclear wastes. In particular, the parameters required for predictive calculations (coefficients of diffusion, surface energy) are still far from being available.

These two theories are in agreement with experimental observations allowing access to the characteristic scales of the critical nuclei and to the experimental follow-up of the nucleation process.

3. Experimental studies of nucleation

3.1. Metastable phases

The occurrence of intermediate metastable phases has been predicted by Ostwald and recently directly observed using *in situ* high resolution transmission electron microscopy (HRTEM) during crystallization of amorphous $LiFePO_4$ (Chung et al., 2009). However, such a possibility was longly studied in binary systems such as Li_2O-SiO_2 (Burgner et al., 2000; Deubener et al., 1993; Iqbal et al., 1998; Soares Jr et al., 2003) or BaO-SiO_2 (Ramsden and James, 1984). Compositional changes were also observed during crystallization of Na_2O-2CaO-3SiO_2 glasses, with the nucleation of aggregates having a composition strongly different from that of the initial phase or from the macroscopic stable phase (Fokin, 2007). This phenomenon seems favor for systems in which a crystalline solid solution is possible (Roskosz, 2005a). The first phases crystallizing in the ternary CaO-Al_2O_3-SiO_2 are never the stable macroscopic phase but the one having a composition close to that of the initial system (congruent crystallization) (Roskosz, 2005a), as predicted by GGA. The first observed crystalline phases present an enrichment in Ca, which is more important as the undercooling increases (Roskosz, 2006). This result is consistent with the important mobility of Ca^{2+} cations and the decoupling (see section 2.2) between the mobility of the cations and the relaxation of the silicate network (Gruener, 2001). The appearance of the first crystalline phases is thus controlled by the diffusion of the most mobile species (Roskosz, 2005b). At large undercooling, the Stokes-Einstein equation is not valid and the relevant transport properties must be taken into account. This is embedded in GGA by distinguishing each atomic diffusion coefficients.

We can note that in the case of an isochemical crystallization (congruent) (Mastelaro et al., 2000), metastable phases are not required. In this case, similarities in the local or medium range order are important to understand homogeneous nucleation (Chen et al., 2010; Chen, 2009; Longstaffe et al., 2008; Mastelaro et al., 2000; Muller et al., 1993; Schneider et al., 2000), since small local atomic reorganization can be involved. Incongruent crystallization implies a more complex mechanism due to the transport of matter over large distances. A correlation between the local cationic environment and the trend to crystallize is not always clear but the medium range organization could promote nucleation (Deubener, 2005). In a similar way, in the presence of nucleating agents, structural arrangements close to the initial crystalline phase were highlighted for the Ti environment in a MgO-Al_2O_3-SiO_2 glass (Guignard et al., 2010; Guignard et al., 2009).

3.2. Homogeneity and heterogeneity of the glass structure

An implicit hypothesis of the CNT is that the initial system is homogeneous. If structural fluctuations preexist, they must be associated with local fluctuations in the parameters determining the thermodynamic barriers. Therefore, they can locally favor the nucleation. These fluctuations are essentially static, with a long life time compared with the time required for an atom to migrate towards the surface of the nucleus. Such static disorder is developed in a DFT nucleation model (Karpov and Oxtoby, 1996).

Heterogeneities are now well documented in colloidal or molecular systems, either experimentally (Anderson and Lekkerkerker, 2002; ten Wolde et al., 1995; Yau and Vekilov, 2001) or by simulations (Kawasaki and Tanaka, 2010). It was shown that a supercooled colloidal liquid does not have an homogeneous disordered structure but contain transient medium range structural order. These regions of high structural order offer low interfacial energies promoting nucleation (Kawasaki and Tanaka, 2010).

Fluctuations have been also recently experimentally observed in glasses and may be intrinsic to their structure (Dargaud et al., 2012; Dargaud et al., 2011) and are present whatever the quenching rate (Dargaud et al., 2012). Such fluctuations can be visualized using STEM-HAADF in Fig. 4 for a ZrO_2-MgO-Al_2O_3-SiO_2 glass: white and dark regions are enriched and depleted with Zr, respectively. The Zr-rich domains can correspond to the intermediate state proposed in GGA or the two-step model. The role of ZrO_2 as a nucleating agent could be explained by an amplification of these fluctuations in the initial state, offering important interfaces between the rich and poor Zr-regions.

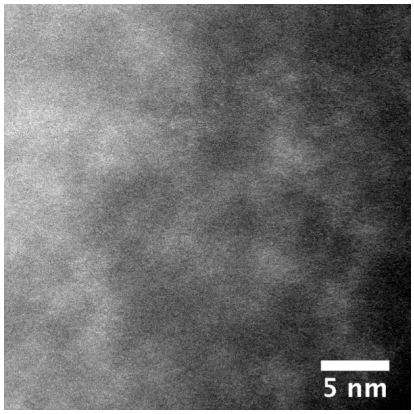

Fig. 4. (a) Images obtained by STEM-HAADF showing direct visualization of heterogeneities in a MgO-Al_2O_3-SiO_2-ZrO_2 glass. White regions correspond to an enrichment with Zr atoms, presenting a diffuse interface with the remaining glass.

3.3. Heterogeneities and phase separation

The extreme case of such heterogeneities can be a L-L separation, preceding a liquid-crystal transformation. Although clearly observed in certain phosphate or borosilicate systems, the phenomenon of phase separation is not a necessary condition for nucleation. The notion of phase separation is not clearly establishes and experimental observation can be ambiguous, particularly at very fine scales (Fig. 5). The same glass (MgO-Al_2O_3-SiO_2 with ZrO_2+ZnO) can be prepared with different quenching rate, giving either an opalescent glass (glass A, slow quenching rate, macroscopically demixed) or a macroscopically homogeneous glass (glass B, fast quenching rate, no opalescence) (Dargaud et al., 2012). In bright field images (Fig. 5a), the glass A presents the characteristic features of phase separation with well defined interfaces between domains. In HAADF mode, the same amorphous-amorphous separation is visible (Fig. 5c) with additional chemical information: the white zones correspond to the high-Z elements, *i.e.* an enrichment in Zr and Zn atoms. For glass B, bright field images suggest a homogeneous material (Fig. 5c). However in HAADF mode (Fig. 5d), heterogeneities are clearly visible with a smaller spatial

extent than for glass A and diffuse interfaces. Such heterogeneities can be intrinsic features of the glass structure or indicate a first stage before macroscopic demixion.

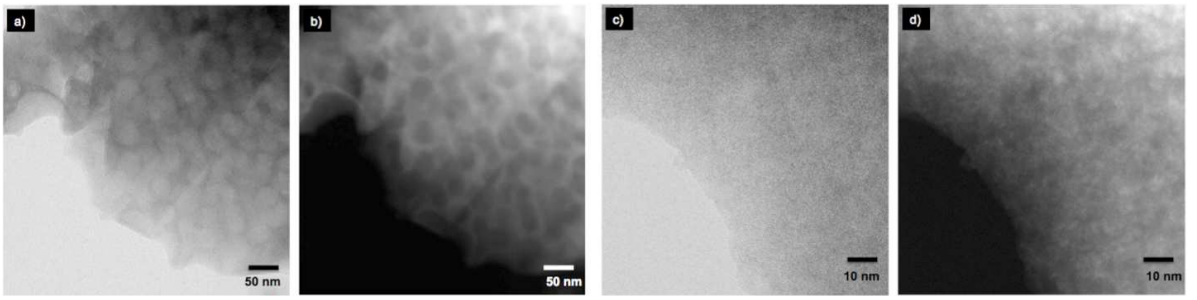

Fig. 5. Micrographs images of a glass with composition 72.43 SiO_2 – 12.91 Al_2O_3 – 7.66 MgO – 2.97 ZnO – 4.03 ZrO_2 (mol.%) obtained by quenching in air, glass A (a, c), or by immersion of the bottom of the crucible in water, glass B (b, d). (a) and (b) Bright field images for glass A and B, respectively. (c) and (d) STEM-HAADF field images for glass A and B, respectively.

3.4. Direct visualization of critical nculei

Directly observing crystal nucleation is difficult. Indeed, once crystal nuclei are big enough to be seen, they are well beyond the critical stage. In the case of glasses, the electronic microscopy is the method of choice for the observation of the initial nuclei. The smallest crystals observed by HRTEM have typically from 2 to 5 nm in diameter (Dargaud et al., 2010; Hoche et al., 2011; Stoch, 2008), without the possibility to assert whether they are critical germs because of the absence of *in situ* experiments allowing the observation of their appearance and disappearance. However, these sizes are in agreement with an estimation of the critical nuclei having several nanometers at high undercooling (Schmelzer et al., 2004). Furthermore, it is possible to observe that these nano-crystals can be not spherical (Fig. 6) (Dargaud et al., 2010). The Fourier transform of fringes on the HRTEM image allows the determination of the nature of these crystalline nanophases. The example in Fig. 6 shows that the zone axis and the diffractogram are consistent with the [100] direction of tetragonal ZrO_2 in a MgO-Al_2O_3-SiO_2 glass (Dargaud et al., 2010) (note that X-ray diffraction would not allow unambiguous interpretation for a 3 nm crystal). The direct observation of the interfaces is unfortunately still challenging.

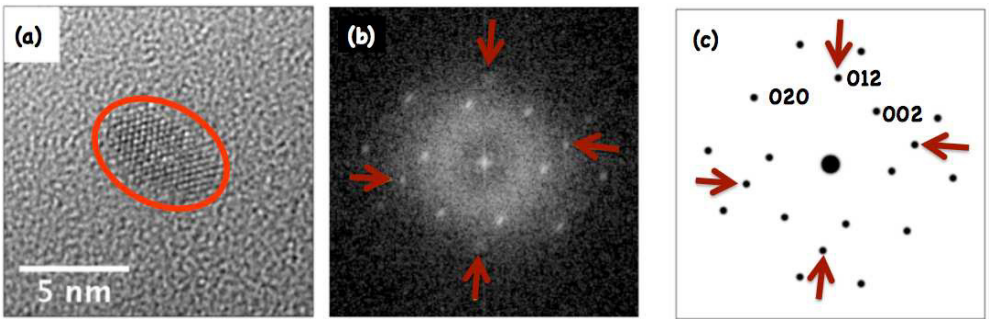

Fig. 6. Evidences of t-ZrO_2 crystalline nanophases in a MgO-Al_2O_3-SiO_2 glass containing 4 mol% ZrO_2 (Dargaud et al., 2010). (a) HRTEM image showing a crystal of 3 nm size. (b) Diffractogram corresponding to fringes in image (a). (c) Simulation of tetragonal ZrO_2 in agreement with image (b) (From (Dargaud et al., 2010)).

3.5. Direct visualization of crystal formation

The STEM-HAADF mode allows a chemical visualization of the appearance of the first crystalline nanophases. As explained in section 3.2, a glass containing 4 mol.% ZrO_2 presents intrinsic inhomogeneities associated to Zr-enriched domains (Dargaud et al., 2011). After heat treatment, the Zr-rich regions become more concentrated with less diffuse borders. Furthermore, it seems that nanocrystals appear at the intersection between these regions by forming crystals with multipodal geometries (Fig. 7). These direct observations allow to propose a scenario for the nucleation in these glasses containing a nucleating agent (Dargaud et al., 2012; Dargaud et al., 2011): in the parent glass, Zr is inhomogenously distributed, with important concentrations in some regions, already presenting a diffuse interface with the rest of the glassy matrix; during the heat treatment, these regions facilitate the diffusion and the concentration of Zr by offering preferential pathways for the Zr mobility; the saturation in Zr favors the nucleation of ZrO_2, due to the presence of interface with the remaining glass; finally, these first nanocrystals grow by following the pathways of Zr diffusion adopting multipodal geometries.

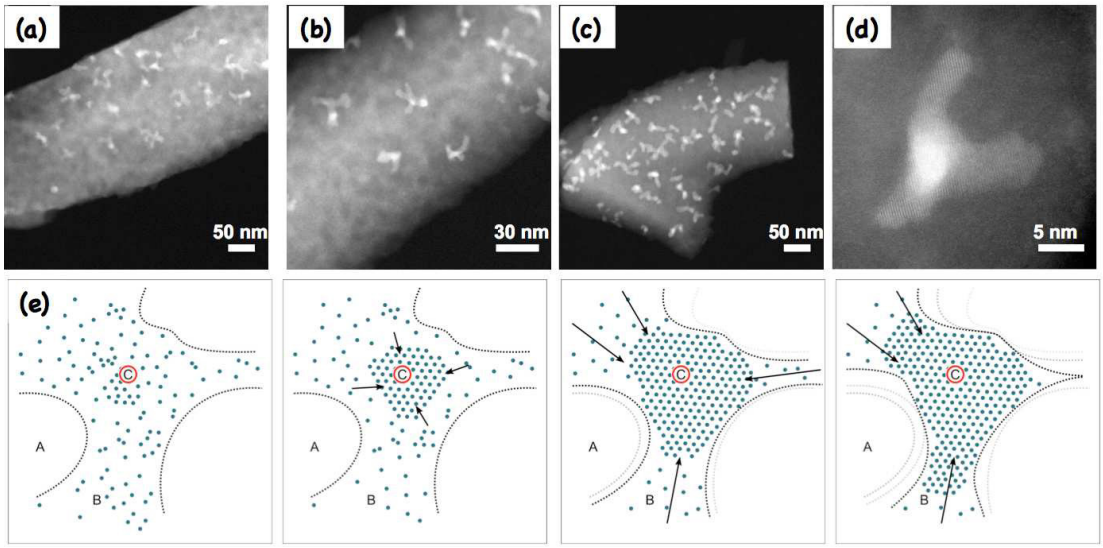

Fig. 7. STEM-HAADF images of a MgO-Al_2O_3-SiO_2 glass containing 4 mol% ZrO_2, with different magnifications (a, b, c). (d) Formation of a crystal with a multipodal geometry. (e) Scenario for the nucleation with distinct domains depleted with Zr (A) or enriched with Zr (B). Intersections of zones B favor formation of ZrO_2 nanocrystals (C). These crystals grow along the Zr diffusion pathways due to domains B (From (Dargaud et al., 2012; Dargaud et al., 2011)).

4. Conclusions

Though implying important tenets, the foundations of the Classical Nucleation Theory have been revaluated during the last decade. The turning point is the direct observation of complex pathways for the formation of thermodynamically stable crystalline phases. These non-classical pathways imply intermediate metastable stages which are now introduced in theoretical approaches (GGA, two-step model). A better knowledge of the nucleation processes is coming from the growing experimental visualization at the (sub-)nanometer scale making possible to follow the atomic reorganization controlling the formation of the initial nuclei. A key finding is the importance of heterogeneities intrinsic to the glass structure, showing the paramount role of medium range organization of the glass (short range is probably less important) on the nuclei formation. Though a predictive model for complex multicomponent materials such as HLW is not yet deliver, today's advances in microscopy and computation should enable us to gain more comprehension of the basic mechanisms that drive nucleation in such systems.

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